IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:	:	PATENT
JAMES B. CREWS	:	
Serial No.: 10/771,563	:	
Filed: February 4, 2004	:	Group Art Unit:
For: AMINOCARBOXYLIC ACID	:	Examiner:
BREAKER COMPOSITIONS FOR	:	Docket No.: 304-27440-USC1
FRACTURING FLUIDS	:	Date: April 19, 2004

DECLARATION UNDER 37 CFR §1.132

Mail Stop Non-Fee Amendment
Assistant Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

In connection with the enclosed Amendment to the above-cited case, please enter the following Declaration in support thereof.

I, JAMES B. CREWS, hereby declare that I am the sole inventor of the methods for breaking the viscosity of polymer gelled aqueous fluids that are the subject of the above-noted patent application;

That in 1980 I earned a Bachelors of Science in geology from Southwest Missouri State University in Springfield, Missouri;

That from 1981 to 1999 I worked at Dowell Schlumberger as a Field Engineer Representative (Fort Smith, Arkansas; Vernal, Utah; and Lake Charles, Louisiana; 1981-1982), Chemist (Mid-Continent Region; 1982-1990), Lab Specialist (Gulf of Mexico Region; 1990-1992), Laboratory Manager (Gulf of Mexico Region; 1992-1999);

I hereby certify that this correspondence, and any attachments referred to, is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to Mail Stop Non-Fee Amendment, Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450, on

APRIL 19, 2004 — Date of Deposit

David L. Mossman — 4/19/2004 — Date

That from 1999 to the present I have worked at Baker Oil Tools, a subsidiary of Baker Hughes Incorporated in Houston, Texas as a Project Scientist (1999-2000), as a Senior Project Scientist (2000-2003), and as a Staff Scientist (2003 to the present);

That I am the co-author with Paul McElfresh of "Deepwater Fracturing: New Challenges, New Fluids," 2002 Deep Offshore Technology Conference Proceedings held November 12-15, 2002, in New Orleans, Louisiana;

That while I have been employed at Baker Oil Tools I have been engaged in research and development of chemicals related to fracturing fluids to improve the recovery of hydrocarbons from subterranean formations;

That I have caused to be performed Examples 8 through 11, described below, which gave the results graphed in FIGS. 8-11 attached hereto;

EXAMPLE 8

The fluid system for the formulations of Example 8 was B9 Emerald FRAQ 30 fluid system plus trisodium salt of hydroxyethylenediaminetetraacetic acid (Na_3HEDTA) or pentasodium salt of diethylenetriaminepentaacetic acid (Na_5DTPA) or no aminocarboxylic acid additive. The Na_3HEDTA was obtained from Akzo Nobel as Dissolvine H-40 (43% bw aqueous solution of Na_3HEDTA). The Na_5DTPA was obtained from Akzo Nobel as Dissolvine D-40 (40% bw aqueous solution of Na_5DTPA). The B9 Emerald FRAQ 30 fluid system is a guar polymer-gelled system available from Baker Oil Tools.

The base fluid was 2 wt% KCl, 0.5 gptg Integra 44 (biocide available from International Specialty Products), 0.4 gptg BA-120LE (organic acid pH buffer), 0.2 gptg N-200E (defoamer), 9.6 gptg WG-1LE (glycol ether based slurry guar product), 2.0 gptg ST-200E (water wetting surfactant), 2.0 gptg NE-200E (non-emulsifier), and 2.0 gptg CS-200E (clay stabilizer). The crosslinker used was XL-1L borate crosslinker available from Benchmark Research (XL-1L has a maximum of 1.1 pounds of borate ions per gallon) along with 1.5 gptg BA-5 (47% bw K_2CO_3). Tests were performed using a Brookfield PVS rheometer at 180°F and 300 psi.

The procedure used for this and Examples 9-11 involved mixing the fluid system in a Waring Blender. The indicated aminocarboxylic acids were added in the indicated

amounts. Control samples of the guar polymer fluid were mixed without adding any aminocarboxylic acid. The samples were tested on the Brookfield PVS rheometer at the indicated temperatures for viscosity differences over time. Modifications to this general procedure are noted.

FIG. 8 shows that 5.0 pptg of Na_3HEDTA and Na_5DTPA had no significant viscosity reduction effect with the B9 Emerald FRAQ 30 fluid system at 180°F over a two hour test period when using 2.0 gptg XL-1L borate crosslinker. When the proportion was increased to 10.0 pptg the Na_3HEDTA and Na_5DTPA still showed no significant effect on the crosslink viscosity with the B9 Emerald FRAQ fluid. The data from FIG. 8 shows how high concentrations of two aminocarboxylic acid chelants, where Na_5DTPA is one of the strongest chelator compounds available, have negligible interaction or complexation with the borate crosslinker ion over a two hour test period at 180°F, even at high chelant to crosslinker by weight ratios.

As FIG. 8 shows, the chelant Na_3HEDTA does not readily complex with the crosslinker or act as a breaker at 180°F *over a two hour test period* but as shown in FIG. 4 *at a more elevated temperature of 220 F* that 5.0 pptg Na_3HEDTA *will readily reduce the fluids viscosity* within one hour. FIGS. 4 and 8 shows *temperature* is an important variable, and that Na_3HEDTA is much more reactive as a breaker at *greater than 180°F fluid temperature.*

EXAMPLE 9

The fluid system for the formulations of Example 9 was again B9 Emerald FRAQ 30 fluid system plus tetrasodium salt of ethylenediaminetetraacetic acid (Na_4EDTA) aminocarboxylic acid additive. The Na_4EDTA was obtained from Akzo Nobel as Dissolvine E-39 (39% bw aqueous solution of Na_4EDTA).

The base fluid was the same as in Example 8. The crosslinker used was again XL-1L along with 2.0 gptg BA-5. Tests were performed using a Brookfield PVS rheometer at 200°F and 300 psi.

FIG. 9 shows that the Na_4EDTA compound *does indeed interact and complex with the XL-1L borate crosslinker ion* within the B9 Emerald FRAQ fluid system at

200°F. The data in FIG. 9 also shows that the aminocarboxylic acid complexation with the borate ion crosslinker can be offset for a period of time by simply increasing the crosslinker concentration. Note how the increase of XL-1L from 2.8 to 4.0 gptg increases the fluid's crosslinked viscosity for at least 5 hours. Note also how the 4.4 gptg XL-1L sample gives less viscosity than the 4.0 gptg XL-1L test sample, and the 4.8 gptg XL-1L gives less viscosity over time than the 4.4 gptg XL-1L sample. That is, the viscosity is maximum at 4.0 gptg.

EXAMPLE 10

The fluid system for the formulations of Example 10 was again B9 Emerald FRAQ 30 fluid system plus 1.25 gptg Na_4EDTA aminocarboxylic acid additive (5.0 pptg), as in Example 9.

The base fluid was the same as in Examples 8 and 9. The crosslinker used was again XL-1L along with 2.0 gptg BA-5, as in Example 9. Tests were performed using a Brookfield PVS rheometer for 24 hours at 200°F and 300 psi. Viscosity measurements were taken after 24 hours at 200°F, and when cooled to 75°F.

FIG. 10 lists the 24 hour viscosity of the fluids tested in FIG. 9. If the Na_4EDTA aminocarboxylic acid chelant compound was reducing viscosity only by complexation with the XL-1L borate crosslinker ions then (1) an increase in crosslinker concentration to an optimum amount should completely offset the viscosity loss due to crosslinker complexation, and (2) the guar polymer should at least show uncrosslinked (linear gel) viscosity at 200°F and when cooled to 75°F.

It should be noted that in borate crosslinked guar fluids, as here, a fluid may appear broken at test temperature, but upon cooling down to room temperature, the fluid may "heal" into a viscous-looking crosslinked gel again. However, test results showed the samples with 5.0 pptg Na_4EDTA to have *no* detection or appearance of any polymer viscosity (crosslinked or uncrosslinked) after 24 hours at 200°F and when cooled to 75°F (in all cases < 3 cps), indicating *significant polymer degradation rather than simply uncrosslinking of the polymer*. All test samples with 5.0 pptg Na_4EDTA, regardless of the amount of XL-1L crosslinker present, had *no* "heal" viscosity when cooled to 75°F, indi-

cating the guar polymer was degraded from about 2,500,000 to less than 300,000 molecular weight. Table I presents the data of FIG. 10 in quantitative form.

TABLE I

Temp.	2.4 gptg XL-1L (no breaker)	2.4 gptg XL-1L	2.8 gptg XL-1L	3.2 gptg XL-1L	3.6 gptg XL-1L	4.0 gptg XL-1L	4.4 gptg XL-1L	4.8 gptg XL-1L
200°F	122	<3	<3	<3	<3	<3	<3	<3
75°F	428	<3	<3	<3	<3	<3	<3	<3

EXAMPLE 11

The fluid system for the formulations of Example 11 was again B9 Emerald FRAQ 30 plus the indicated amounts of Na_4EDTA aminocarboxylic acid additive.

The base fluid was the same as in Examples 8 and 9. The crosslinker used was again XL-1L along with 1.0 gptg BA-5. Tests were performed using a Brookfield PVS rheometer at 75°F and 300 psi.

FIG. 11 shows that 1.4 gptg XL-1L gives overall better and stronger crosslinked viscosity at 75°F versus the use of 1.2 gptg XL-1L. FIG. 11 additionally shows that with the *lower* amount of crosslinker (1.2 gptg XL-1L) the presence of 5.0 pptg and 10 pptg Na_4EDTA slightly *increases* the crosslinked viscosity rather than *reducing* the fluid's viscosity as would be expected, and the addition of Na_4EDTA up to 10.0 pptg at 75°F shows that *no significant or noticeable sequestering or complexation with the borate crosslinker ion at this lower temperature*. Typically, aminocarboxylic acids have a slightly higher stability constant for cations at lower temperatures than at elevated temperatures (Dow Chemical Company publication, *Keys To Chelation,* Section II. E. 1, 1969, Midland, Michigan).

Further, I hereby declare:

That FIG. 8 shows how two aminocarboxylic acids (Na_3HEDTA and Na_5DTPA) do not readily form complexes with borate ions, at least at 180°F within 2 hours, and FIG. 11 shows the same for one aminocarboxylic acid (Na_4EDTA) at 75°F within 1 hour;

That FIGS. 9 and 10 together show that when an aminocarboxylic acid chelant does interact with the borate ion, such as Na_4EDTA at 200°F, the complexation is for a rather short period of time and such interaction does not prevent the guar polymer chain itself from degradation;

That the interaction seen in FIG. 9 between the Na_4EDTA and XL-1L is not a complete, permanent, or long-term sequestering or complexation, and that FIG. 9 shows that increasing the amount of crosslinker will to a degree offset crosslinker sequestering-complexation with the aminocarboxylic acid present, but continued increase in amount of crosslinker will eventually result in *lower* viscosity and "over crosslinking" of the guar polymer; and that a stable crosslinked polymer cannot be achieved by simply increasing and/or optimizing the crosslinker concentration when 5.0 pptg Na_4EDTA is present in the B9 Emerald FRAQ fluid at 200°F;

That FIG. 10 shows how increase in crosslinker concentration will not prevent the polymer chain degradation with Na_4EDTA present, and that FIGS. 9 and 10 show how the increased amount of crosslinker (such as the 4.0 gptg XL-1L loading) apparently will only slow the degradation rate down a small amount (a few hours) during the first 8 or so hours the fluid is kept at 200°F, but will not prevent the evidence of significant polymer chain degradation when the fluid has been kept at 200°F for 24 hours;

That in borate crosslinked guar fluids, the type used here, a fluid may appear broken at test temperature, but upon cooling down to room temperature, the fluid may "heal" into a viscous-looking crosslinked gel;

That one having ordinary skill in the art would expect that if permanent sequestering or complexation of the borate ions would occur then increasing the crosslinker concentration would eventually tie up most all of the aminocarboxylic acid chelant and a stable crosslinked fluid could be achieved and little if any aminocarboxylic acid would then be available for any further uncrosslinking of the polymer and/or breaking of the polymer chain; however, this is not the case, as FIG. 10 shows that all test samples with

5.0 pptg Na_4EDTA, regardless of the amount of XL-1L crosslinker present, showed no crosslinked or uncrosslinked viscosity after 24 hours at 200°F or when cooled to 75°F;

That the sample in FIG. 10 using 2.4 gptg XL-1L crosslinker and no breaker (no Na_4EDTA present) showed noticeable crosslinked viscosity after 24 hours at 200°F and an increase in crosslink viscosity when cooled to 75°F due to the healing phenomenon, that, however, no such healing phenomenon occurred in any of the other systems, indicating degradation of the polymer backbone itself; and

That FIG. 11 shows that 5.0 pptg and even 10.0 pptg Na_4EDTA do not appear to sequester any noticeable amount of borate ions at the considerably lower temperature of 75°F over a 1 hour period, even with the use of a relatively low amount of borate crosslinker (1.2 gptg XL-1L has about 1.32 pounds of available borate ions); and

That this data thus demonstrates the breaking of the viscosity of polymer gelled aqueous fluids comprising a crosslinked guar or derivatized guar polymer gel by using an effective amount of at least one aminocarboxylic acid within an optimum fluid temperature range to break down the gel by acting on the crosslinker but primarily acting directly on the polymer gel, as claimed.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application cited above or any patent issued thereon.

Further Declarant sayeth not.

Signature of Declarant: ____________________
JAMES B. CREWS

Date: April 19, 2004